

**ORGANO-RUTHENABORANE AND -OSMABORANE CLUSTER
 COMPOUNDS: PREPARATION AND NMR STUDIES OF [6-(η^6 -C₆Me₆)-*nido*-6-MB₉H₁₃] (M = Ru, Os) AND THE REARRANGED CLUSTER [5-(η^6 -C₆Me₆)-*nido*-5-RuB₉H₁₁-7-(PMe₂Ph)] ***

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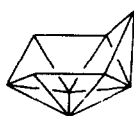
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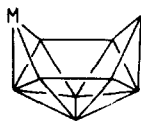
Summary

Reaction of the versatile organometallaborane synthon $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ with *arachno*-[B₉H₁₄][−] affords [6-(η^6 -C₆Me₆)-*nido*-6-RuB₉H₁₃] in 80% yield. An analogous reaction with $[(\eta^6\text{-C}_6\text{Me}_6)\text{OsCl}_2]_2$ (here reported for the first time) gives [6-(η^6 -C₆Me₆)-*nido*-6-OsB₉H₁₃] in 13% yield. Treatment of the *nido*-6-ruthenadecaborane cluster with tertiary phosphines results in rearrangement and formation of [5-(η^6 -C₆Me₆)-*nido*-5-RuB₉H₁₁-7-PR₃] (77% yield for PR₃ = PMe₂Ph; 54% yield for PPh₃). The metallaborane products are all yellow or orange-yellow air-stable crystalline compounds which have been characterized by elemental analysis, mass spectrometry, and multi-element, multiple resonance, and 2D NMR spectroscopy.

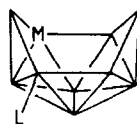
We have recently found that the organorhodium species $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$ reacts readily with polyhedral borane anions to form pentamethylcyclopentadienylrhodaboranes in good yields [1–3]. For example, it reacts with the *arachno* nine-vertex anion iso-[B₉H₁₄][−] (gross B₉ configuration I) to form [6-(η^5 -C₅Me₅)-*nido*-6-RhB₉H₁₃] (gross MB₉ configuration II) [1], and we have also found that this resulting ten-vertex *nido*-6-metalladecaborane reacts with the tertiary phosphine PMe₂Ph to give, inter alia, the rearranged *nido*-rhodadecaborane [5-(η^5 -C₅Me₅)-



(I)



(II)



(III)

* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

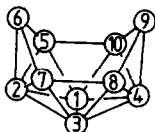
TABLE 1

MEASURED NMR PARAMETERS FOR $[6-(\eta^6-C_6Me_6)\text{-}nido\text{-}6\text{-}RuB_9H_{13}]^a$, $[6-(\eta^6-C_6Me_6)\text{-}nido\text{-}6\text{-}OsB_9H_{13}]^a$, AND, FOR COMPARISON PURPOSES, DATA FOR $[6-(\eta^5-C_5Me_5)\text{-}nido\text{-}6\text{-}RhB_9H_{13}]^b$

Assign- ment ^c	$[nido\text{-}6-(\eta^6-C_6Me_6)RuB_9H_{13}]$ (1)		$[nido\text{-}6-(\eta^6-C_6Me_6)OsB_9H_{13}]$ (2)		$[nido\text{-}6-(\eta^5-C_5Me_5)RhB_9H_{13}]$ in CD_2Cl_2 at 298 K ^b		
	$\delta(^{11}B)$ (ppm) ^d	$J(^{11}B\text{-}^1H)$ (Hz) ^e	$\delta(^1H)$ (ppm) ^f	correlations observed ^g	$\delta(^{11}B)$ (ppm) ^d	$J(^{11}B\text{-}^1H)$ (Hz) ^e	$\delta(^1H)$ (ppm) ^f
1,3	+13.7 (2B)	137	+3.68 (2H)	2s 4m 5.7s 8,10m 5,6; 6,7s 8,9;9,10s	+12.0	137	+12.7
2	-16.6 (1B)	139	+0.37 (1H)	1,3s 5,7w	-27.1	139	-10.8
4	-30.7 (1B)	150	+1.12 (1H)	1,3s 9m 8,10m 8,9;9,10m	-31.6	152	-30.6
5,7	+22.0 (2B)	162	+4.29 (2H) ^h	1,3s 2w 8,10w 5,6;6,7s ²	+19.8	140	+19.4
6	[Rh]	-	[+2.28 (18H)] ⁱ	-	[Os]	-	[+2.31] ⁱ
8,10	-1.1 (2B)	152	+2.77 (2H) ^j	1,3m 4m 5,7w 8,9;9,10s ²	-2.1	151	-0.9
9	+5.0 (1B)	158	+3.29 (1H) ^j	4m 8,9;9,10s ²	+5.9	155	+4.7
5,6;6,7	-	^k	-10.05 (2H) ^h	1,3s 5,7s ² 8,9;9,10m ²	-	^k	-
8,9;9,10	-	^k	-3.12 (2H) ^j	1,3s 4m 8,10s ² 5,6;6,7m ²	-	^k	-

^a This work. ^b Data from ref. 1. ^c Assignment by relative intensities, $^1H\text{-}(^{11}B\text{selective})$, 2D $[^{11}B\text{-}^{11}B]$ -COSY, and 2D $[^1H\text{-}^1H]$ -COSY spectroscopy, and comparison with other *nido*-6-metalladecaboranes (refs. 1, 19, 24-26, 30), numbering as in structure IV and Fig. 1. ^d ± 0.5 ppm to high frequency (low field) of $[BF_3(OEt_2)]$ in $CDCl_3$; $[^{11}B\text{-}^{11}B]$ -COSY correlations were essentially the same as those reported for the rhodium analogue [1]. ^e ± 8 Hz; measured from ^{11}B spectra with resolution enhancement to achieve baseline separation of doublet components. ^f ± 0.05 ppm to high frequency (low field) of TMS; 1H resonances related to directly bound B atom positions by selective $^1H\text{-}(^{11}B)$ experiments. ^g Measured with $\{^{11}B(\text{broad-band noise})\}$ decoupling; experimental and data-processing parameters are given in Table 3; s, strong; w, weak; m, intermediate; numerical superscripts refer to n in $nJ(^1H\text{-}^1H)$; lack of superscript indicates $n = 3$. ^h Irradiation at $\nu[^{11}B(5,7)]$ sharpens $\delta[^1H(5,7)]$ and $\delta[^1H(5,6;6,7)]$. ⁱ C_nMe_n resonances. ^j Irradiation in region of $\nu[^{11}B(8,10)]$ and $\nu[^{11}B(9)]$ sharpens $\delta[^1H(8,9;9,10)]$ as well as $\delta[^1H(8,10)]$ and $\delta[^1H(9)]$. ^k Any $J(^{11}B\text{-}^1H_n)$ not resolved.

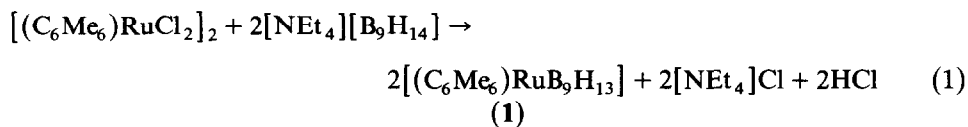
nido-5-RhB₉H₁₁-7-(PMe₂Ph)] (gross configuration III) [2]. It is apparent that the isoelectronic organo-ruthenium and -osmium halides [(η⁶-C₆Me₆)MCl₂]₂ (M = Ru, Os) have a similar versatility to that of [(η⁵-C₅Me₅)RhCl₂]₂ as organometal-laborane synthons [4] and we have therefore examined their reactions with [B₉H₁₄]⁻. Of the products, the ruthenaborane [6-(η⁵-C₆Me₆)-*nido*-6-RuB₉H₁₃] is formed in high yield and this permits the ready examination of its further chemistry, particularly its reaction with the tertiary phosphines PMe₂Ph and PPh₃. Some preliminary [4] and related [5,6] aspects of hexamethylbenzeneruthenaborane chemistry have been reported elsewhere. The *nido*-decaborane numbering system, as used in this paper, is in structure IV.



(IV)

Results and Discussion

The reaction between [(η⁶-C₆Me₆)RuCl₂]₂ and [NEt₄][B₉H₁₄] in dichloromethane solution for 18 h at room temperature, followed by chromatographic separation, resulted in the isolation of an 80% yield of [6-(η⁶-C₆Me₆)-*nido*-6-RuB₉H₁₃] (compound **1**):



Chromatography also revealed a number of other yellow, orange, and red minor compounds (≤ ca. 1% yield) which were either too unstable or formed in a too small yield to encourage further detailed investigation. However, NMR studies suggested that some of these might have novel metallaborane cluster configurations which would repay further study in due course.

The main product **1**, an air stable orange crystalline solid, was identified by elemental analysis, mass spectrometry, and NMR spectroscopy. The measured NMR parameters are in Table 1, together with those of the previously reported rhodaborane [6-(η⁵-C₅Me₅)-*nido*-6-RhB₉H₁₃] [1] for comparison. The close correspondence of the ¹¹B shielding patterns and the ¹H shielding patterns for the two compounds, and their interrelationship (see also below near Figs. 3 and 4), readily identify the new ruthenaborane **1** as a *nido*-6-metalladecaborane, and the incidence of an essentially unmodified η⁶-C₆Me₆ grouping on the metal is also apparent from proton NMR spectroscopy. The identification of **1** as [6-(η⁶-C₆Me₆)-*nido*-6-RuB₉H₁₃] is also consistent with the 70 eV EI mass spectrum in which the high-mass "cut-off" occurs at *m/e* = 378, corresponding to the highest isotopomer of the molecular ion [(C₆Me₆)RuB₉H₁₃]⁺. The mass spectrum also exhibits typical but non-extensive sequential loss of H and/or BH units from the molecular ion, some metastable-supported. The only other feature of note in the mass spectrum was the rather high

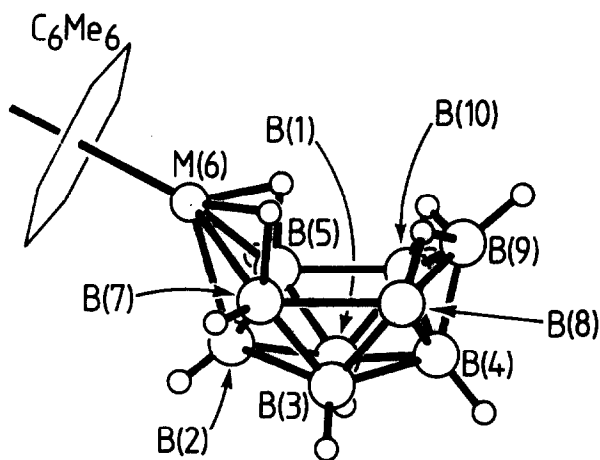
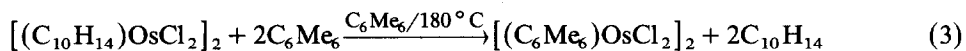
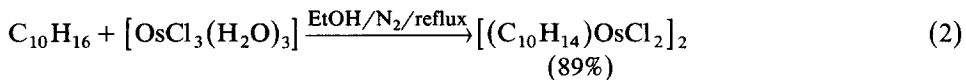


Fig. 1. Proposed molecular structure of $[6(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-6-MB}_9\text{H}_{13}]$, where $M = \text{Ru}$ (compound 1), Os (compound 2).

incidence of doubly-charged fragments corresponding to $[\text{C}_6\text{Me}_6\text{RuB}_n\text{H}_x]^{2+}$ ($n = 8, 9$) near m/e ca. 180.

A representation of the proposed structure is in Fig. 1. The $\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\}$ moiety subrogates the 6-BH position in the parent *nido*-decaborane, $\text{B}_{10}\text{H}_{14}$, and can therefore be regarded as a straightforward two-electron three-orbital contributor to the metallaborane cluster, consistent with the Wade-Williams electron-counting and cluster geometry rules [7,8], and consistent with the description of the compound as an eighteen-electron d^6 ruthenium(II) complex. In cluster terms the compound can be thought of as a *nido*-6-metalladecaborane cluster conjoined to a *nido*-1-metallaheptacarbane cluster at the common metal atom. The compound can also be regarded as having sandwich character since the $\eta^6\text{-C}_6$ plane and the B(2)B(5)B(7) plane are expected to be nearly parallel.

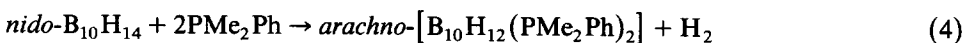
It was of interest to see whether this high-yield synthesis could be extended to the osmium analogue $[6-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-6-OsB}_9\text{H}_{13}]$ (compound 2) using the analogous organoosmium starting halide $[(\eta^6\text{-C}_6\text{Me}_6)\text{OsCl}_2]_2$. As far as we know, when we started this work [4] this potentially useful reagent had not previously been reported, but we found that a preparative route analogous to that [9] for $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ via α -phellandrene and a *p*-cymene complex (eq. 2 and 3), works also for the osmium complex though in somewhat lower yields (ca. 30%):



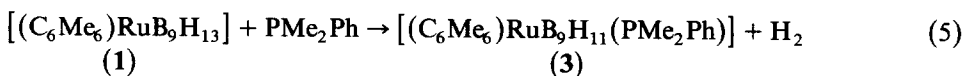
In these equations $\text{C}_{10}\text{H}_{16}$ is α -phellandrene (5-isopropyl-2-methyl-1,3-cyclohexadiene) and $\text{C}_{10}\text{H}_{14}$ is *p*-cymene (1-isopropyl-4-methylbenzene). The principal difference between the ruthenium and osmium preparations is in the extraction procedure (see Experimental).

Reaction of $[(\eta^6\text{-C}_6\text{Me}_6)\text{OsCl}_2]_2$ with $[\text{B}_9\text{H}_{14}]^-$ under similar conditions to that of eq. 1 above resulted in the formation of the corresponding *nido*-6-osmadecaborane $[6-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-6-OsB}_9\text{H}_{13}]$ (compound **2**, Fig. 1), again readily identified by comparative NMR spectroscopy (Table 1, and Figs. 3 and 4) and mass spectrometry. The isolable yield of the red-orange crystalline solid was, however, more modest (ca. 13%) and again the reaction produced a variety of coloured by-products in small yield which we have not yet been able to characterize. Nevertheless the reaction augurs well for an extensive and interesting osmaborane cluster chemistry based on the $\{(\text{C}_6\text{Me}_6)\text{Os}\}$ moiety which should complement the known and continually expanding metallaborane chemistry based on the $\{(\text{C}_6\text{Me}_6)\text{-Ru}\}$ [4–6] $\{(\text{C}_5\text{Me}_5)\text{Co}\}$ [10–15], and $\{(\text{C}_5\text{Me}_5)\text{Rh}\}$ [1–3, 16] units.

The high yield of the *nido*-6-ruthenadecaborane cluster **1** from readily synthesized starting materials enables its chemistry to be further investigated. The parent borane, $\text{B}_{10}\text{H}_{14}$, has an extensive chemistry and it was of interest to see the extent to which its known reactions were paralleled or modified with the organoruthenium-subrogated cluster **1**. For example, $\text{B}_{10}\text{H}_{14}$ is known to react essentially quantitatively with nucleophiles such as tertiary phosphines to form *arachno*-6,9-bis(ligand) adducts such as $[\text{B}_{10}\text{H}_{12}(\text{PMe}_2\text{Ph})_2]$; the reaction is spontaneous and exothermic in neutral dipolar solvents at room temperature [17,18]:



By contrast, compound **1** does not react immediately under these conditions but, on mild heating, gives a yellow crystalline compound formulated as $[5-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-5-RuB}_9\text{H}_{11}\text{-7-(PMe}_2\text{Ph)}]$ (**3**):



According to this scheme, only one two-electron phosphine ligand adds to the cluster and the “two-electron” species dihydrogen is eliminated: the *nido* ten-vertex cluster-electron count is thereby retained [7] though the resulting *nido* cluster has undergone rearrangement. This should be compared with eq. 4 where addition of the second mole of phosphine effects the cluster conversion from *nido* to *arachno*.

Compound **3** was identified by NMR spectroscopy, elemental analysis, and mass spectrometry. Measured NMR parameters are given in Table 2. Nine separate boron-atom positions are apparent, of which eight bear *exo*-terminal hydrogen atoms, and the ninth an *exo*-terminal phosphorus atom which ^{31}P and ^1H NMR spectroscopy show is associated with a PMe_2Ph grouping. There are in addition three bridging hydrogen atoms, one associated with a high-field $\delta(^1\text{H})$ value indicative of M–H–B bridging. These considerations, together with selective $^1\text{H}\text{-}\{^{11}\text{B}\}$ spectroscopy and the connectivity information available from $^{11}\text{B}\text{-}^{11}\text{B}$ - and $^1\text{H}\text{-}^1\text{H}$ -COSY experiments (also summarised in Table 2; see also Fig. 3 below), indicated a *nido*-5-metalladecaborane configuration, with PMe_2Ph bound to the 7-position instead of *exo*-hydrogen, and without a bridging hydrogen atom. This suggested the formulation $[5-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-5-RuB}_9\text{H}_{11}\text{-7-(PMe}_2\text{Ph)}]$, consistent with the NMR spectroscopic similarity to the $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}\}$ analogue (also included in Table 2 for comparison) [2], and also with the results of 70 eV E.I. mass spectrometry, which gave a high-mass “cut-off” corresponding to the highest $[(\text{C}_6\text{Me}_6)\text{RuB}_9\text{H}_{11}(\text{PMe}_2\text{Ph})]^+$ isotopomer. As with compound **1** there were signifi-

TABLE 2

MEASURED NMR PARAMETERS FOR [5-(η^6 -C₆Me₆)-*nido*-5-RuB₉H₁₁-7-(PMe₂Ph)] (3)^a, [5-(η^6 -C₆Me₆)-*nido*-RuB₉H₁₁-7-PPh₃] (4)^a AND, FOR COMPARISON PURPOSES, DATA FOR [5-(η^6 -C₅Me₅)-*nido*-5-RhB₉H₁₁-7-(PMe₂Ph)] (3)^b

Assign- ment ^c	[(C ₆ Me ₆)RuB ₉ H ₁₁ (PMe ₂ Ph)] (3)		[(C ₆ Me ₆)RuB ₉ H ₁₁ (PPh ₃)] (4) ^{a,c}		[(C ₅ Me ₅)RhB ₉ H ₁₁ (PMe ₂ Ph)] ^b					
	$\delta(^{11}\text{B})$ (ppm) ^d	$J(^{11}\text{B}-^1\text{H})$ (Hz) ^e	$\delta(^1\text{H})$ (ppm) ^f	Observed 2D COSY correlations [¹¹ B- ¹ H] ^{g,h}	$\delta(^{11}\text{B})$ (ppm) ^d	$\delta(^1\text{H})$ (ppm) ^f	$\delta(^{11}\text{B})$ (ppm) ^d	$\delta(^1\text{H})$ (ppm) ^f	$\delta(^{11}\text{B})$ (ppm) ^d	$\delta(^1\text{H})$ (ppm) ^f
1	+2.4	130	+2.07	2s 3m 4w 10m?	+2.4	+2.06	+6.0	+2.38	+6.0	+1.81 ⁱ
2	-0.6	133	+1.18	1s 6w ^h	ca. 0.0 ^j	+1.39	+4.3	+1.54	+4.3	+6.37
3	-2.9	^k	+1.97	1m 4s 7w? 8s ^h	-2.65	+2.14	-2.0	+1.90	-2.0	+1.76
4	-42.7	139	+0.07	1w 3s 8w 9s 10w	-42.8	+0.01	-42.1	-0.04	-42.1	+2.06
5	[Ru]	-	[+2.08] ^l	(8,9)s (9,10)s	[Ru]	[+2.06] ^l	[Rh]	[+1.81] ^l	[Rh]	[+1.81] ^l
6	+63.0	^k	+6.27	- ^m	+63.9	+6.23	+64.0	+6.37	+64.0	+6.37
7	-8.2	ⁿ	[PMe ₂ Ph] ⁿ	3w? 6w	ca. -8.0 ^o	[PPh ₃] ^p	-7.6	[PMe ₂ Ph] ^q	-7.6	[PMe ₂ Ph] ^q
8	-9.1	^k	+1.67	3s 4w	ca. -8.0 ^o	+1.69	-7.0	+1.76	-7.0	+1.76
9	-18.7	156	+1.98	4s	-19.0	+1.98	-17.5	+2.06	-17.5	+2.06
10	-1.7	137	+3.01	1m? 4w	ca. 0.0 ^j	+3.02	+0.6	+3.01	+0.6	+3.01
5,6(bridge)	-	-	-17.51	- ^r	-	-17.57	-	-14.81	-	-14.81
8,9(bridge)	-	-	-3.68	[3/9]s ^r 4s 8m 10s (9,10)s	-	-3.47	-	-3.33	-	-3.33
9,10(bridge)	-	-	-2.25	1s [3/9]s ^r 4s 8s 10m (9,10)s	-	-2.22	-	-1.91	-	-1.91

^a This work. ^b Data from ref. 2. ^c Assignments by ¹H-¹¹B(selective), 2D [¹¹B-¹¹B(selective)], 2D [¹¹B-¹¹B]COSY, and 2D [¹H-¹¹H]COSY experiments and by analogy with [(C₅Me₅)RhB₉H₁₁(PMe₂Ph)] (last two columns and ref. 2). ^d ± 0.5 ppm to high frequency (low field) of [BF₃(OEt₂)] in CDCl₃. ^{e,f} See footnotes e,f in Table 1. ^g Conditions as in Table 3; see also footnote g in Table 1. ^h Note any ¹¹B(2)-¹¹B(3) correlation not observable due to proximity of peaks. ⁱ Note ¹H(3) and ¹H(9) resonances coincident under these conditions and so their individual correlations are indistinguishable. ^j Note ¹¹B(2) and ¹¹B(10) resonances accidentally near-coincident. ^k Not resolved. ^l C_nMe_n resonances. ^m Not observed, see caption to Fig. 3. ⁿ $\delta(^{31}\text{P})$ -0.1 ppm, $J(^{31}\text{P}-^{11}\text{B})$ not resolved due to disadvantageous overlap of ¹¹B(7) and ¹¹B(8) resonances. ^o Note ¹¹B(7) and ¹¹B(8) resonances accidentally near-coincident. ^p $\delta(^{31}\text{P})$ +17.9 ppm, $J(^{31}\text{P}-^{11}\text{B})$ obscured (see footnote o). ^q $J(^{31}\text{P}-^{11}\text{B})$ ca. 143 Hz. ^r No correlations apparent.

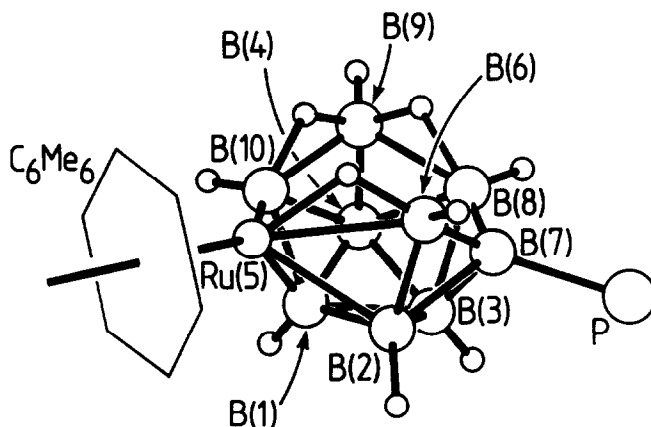


Fig. 2. Proposed structure of $[5-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-5-RuB}_9\text{H}_{11}\text{-7-(PR}_3)]$, where $\text{PR}_3 = \text{PMe}_2\text{Ph}$ (compound 3), PPh_3 (compound 4). P-Organyl groups have been omitted for clarity and in this projection the *exo*-terminal H atom on B(4) is obscured.

cant mass spectroscopic fragments corresponding approximately to a doubly charged molecular ion, but now also some fragmentation involving loss of PMe_2Ph from the $[(\text{C}_6\text{Me}_6)\text{RuB}_9\text{H}_n(\text{PMe}_2\text{Ph})]^+$ cluster was also apparent.

Also included in Table 2 are NMR data for the triphenylphosphine analogue $[5-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-5-RuB}_9\text{H}_{11}\text{-7-(PPh}_3)]$ (compound 4). This was isolated from a reaction analogous to that used for the preparation of compound 3, but by using PPh_3 instead of PMe_2Ph as the starting phosphine. The same product 4 was isolated in small yield from the attempted reaction between $[\text{PtCl}_2(\text{PPh}_3)_2]$ and compound 1 in the presence of base in an attempt to prepare polyhedral platinum-ruthenadecaborane species.

A representation of the proposed structure of compound 3 is given in Fig. 2. This is interpretable in terms of a $\text{B}_{10}\text{H}_{14}$ *nido*-decaborane skeleton in which the $\text{BH}(\text{exo})$ unit in the 5-position has been subrogated by an isoelectronic and isolobal $\{\text{Ru}(\text{C}_6\text{Me}_6)\}$ moiety and the $\text{BH}(\text{exo})$ unit in the 7-position by the isolobal $\{\text{B}(\text{PMe}_2\text{Ph})\}$ unit. The net positive charge that this latter subrogation would introduce is removed by the notional deprotonation at the *nido*-decaboranyl B(6)–B(7) position. Compound 3 therefore bears some similarities to the previously reported [19] *nido*-6-ruthenadecaborane $[(\text{CO})(\text{PPh}_3)_2\text{RuB}_9\text{H}_{11}(\text{PPh}_3)]$ which however has the metal centre attached to phosphine and carbonyl ligands instead of the C_6Me_6 ligand of compound 3. As with compound 1 above, compound 3 can also be regarded as an “octahedral” 18-electron ruthenium(II) complex, and the cluster configuration is entirely in accord with the Wade–Williams rules [7,8].

A number of aspects arising from the detailed NMR spectroscopic investigations of compounds 1–4 merit brief mention. The techniques of ^{11}B – ^{11}B [20] and ^1H – ^1H –COSY [21] NMR spectroscopy as applied to polyhedral boron compounds are still relatively new, and in the ^{11}B – ^{11}B work it is of interest that the correlations observed for compound 3 (Table 2), although qualitatively similar to those for the rhodaborane analogue, [2] appear to exhibit subtle differences in intensity to the latter compound. Intensity variations of the correlations, both

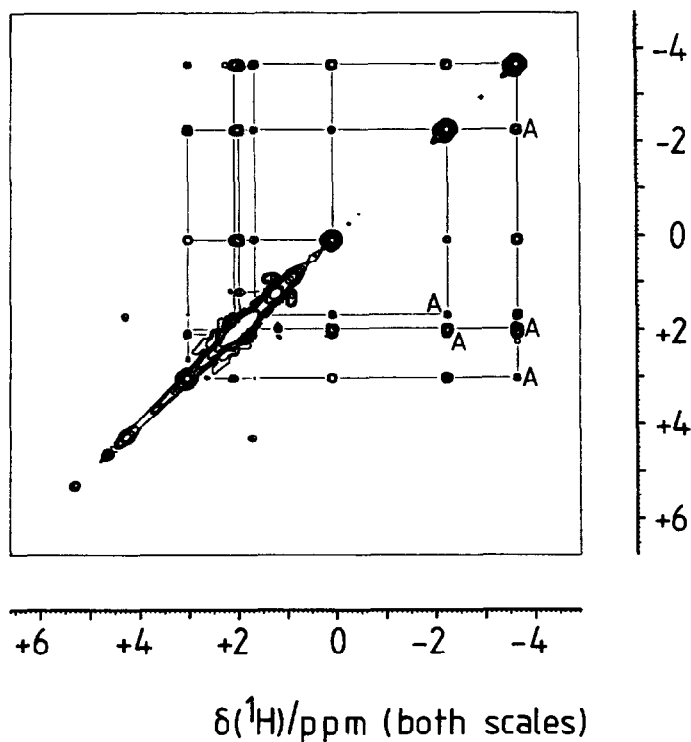


Fig. 3. A 2D [^1H - ^1H]-COSY NMR contour plot for a sample of compound **3** in CDCl_3 solution at ca. 304 K, recorded under conditions of $\{^{11}\text{B}$ (broad band noise) $\}$ decoupling. The ^1H resonance of BH(6) at δ +6.27 was insufficiently decoupled to appear on the plot, and ^1H (5,6) (off-scale at -17.51 ppm) did not exhibit any cross-peaks with the other proton resonances. Correlations arising from $^2J(^1\text{H}-\text{B}-^1\text{H})$ paths (designated A) are on the lower right-hand diagonal half; the other correlations arise from $^3J(^1\text{H}-\text{B}-\text{B}-^1\text{H})$.

within a compound, or among series of compounds, will reflect differences in interboron spin-spin coupling constants, and we are finding these of increasing diagnostic use in our organometallaborane work [3,22]. It should however be emphasized that the intensity of the interboron correlations will depend upon relaxation times as well as coupling constants [3,23], and so comparable solution motional conditions are required for absolute comparisons.

The interproton correlations in the [^1H - ^1H]-COSY work (Fig. 3) are also illustrative of points that will probably become recognised as being general ones, in particular (a) certain interproton correlations arising from $^3J(^1\text{H}-\text{B}-\text{B}-^1\text{H})$ coupling paths are apparent when the corresponding $^1J(^{11}\text{B}-^{11}\text{B})$ interboron ones are absent (e.g. between the B(5) and B(10) positions in compound **1** (Table 1)), and (b) a number of correlations arising from $^2J(^1\text{H}-\text{B}-^1\text{H})$ involving bridging hydrogen atoms are also apparent. These latter are of particular use in assigning bridging hydrogen positions and thence structural type [21]. As with the interboron correlations, there is significant variation in the intensities of the observed interproton correlations, reflecting variations in the magnitudes of the corresponding couplings $^nJ(^1\text{H}-^1\text{H})$, which also is likely to be of increasing diagnostic use [22].

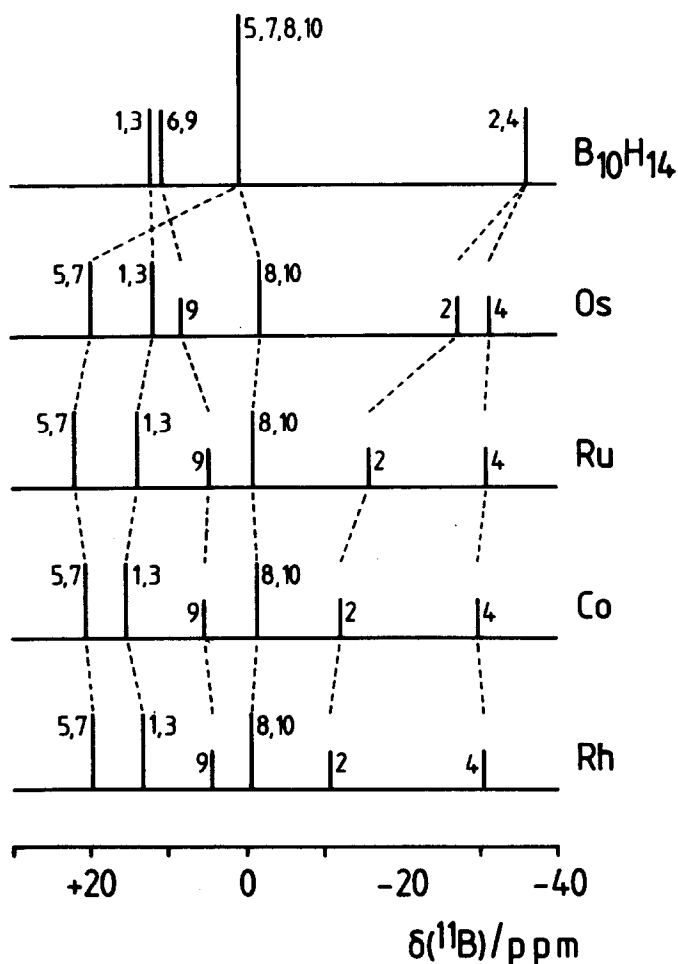


Fig. 4. Stick diagram of the ^{11}B NMR positions for $\text{B}_{10}\text{H}_{14}$, $6\text{-}[(\text{C}_6\text{Me}_6)\text{OsB}_9\text{H}_{13}]$ (compound 2, designated "Os"), $6\text{-}[(\text{C}_6\text{Me}_6)\text{RuB}_9\text{H}_{13}]$ (compound 1, designated "Ru"), $6\text{-}[(\text{C}_5\text{Me}_5)\text{CoB}_9\text{H}_{13}]$ (designated "Co", data from ref. 13), and $6\text{-}[(\text{C}_5\text{Me}_5)\text{RhB}_9\text{H}_{13}]$ (designated "Rh", data from ref. 1). The B(2) and B(5,7) resonance positions of the metallaboranes are in general considerably downfield from those of $\text{B}_{10}\text{H}_{14}$, (compare ref. 25), whereas the other positions remain relatively unaffected.

Apparent from the detailed assignments of the ^{11}B and ^1H spectra for the compounds in Tables 1 and 2 are the extreme similarities of the shielding patterns for compounds of the same structural type as the metal centre is varied among a variety of different arene metal units. Figure 4 summarizes the ^{11}B data for the *nido*-6 metalladecaboranes 1 and 2, and also includes their $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Co}\}$ and $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}\}$ analogues for comparison (data from refs. 1 and 13). The relationship to the shielding pattern of $\text{B}_{10}\text{H}_{14}$ itself is readily traced, and it is apparent that this general shielding pattern is retained for the metallaboranes, except for the B(2) and B(5,7) positions immediately next to the metal centres which are considerably deshielded. This is in contrast to the recently reported series of *nido*-6-metalladecaboranes in which the metal centre varies from $\{(\text{PMe}_2\text{Ph})_3\text{H}_2\text{W}\}$, via

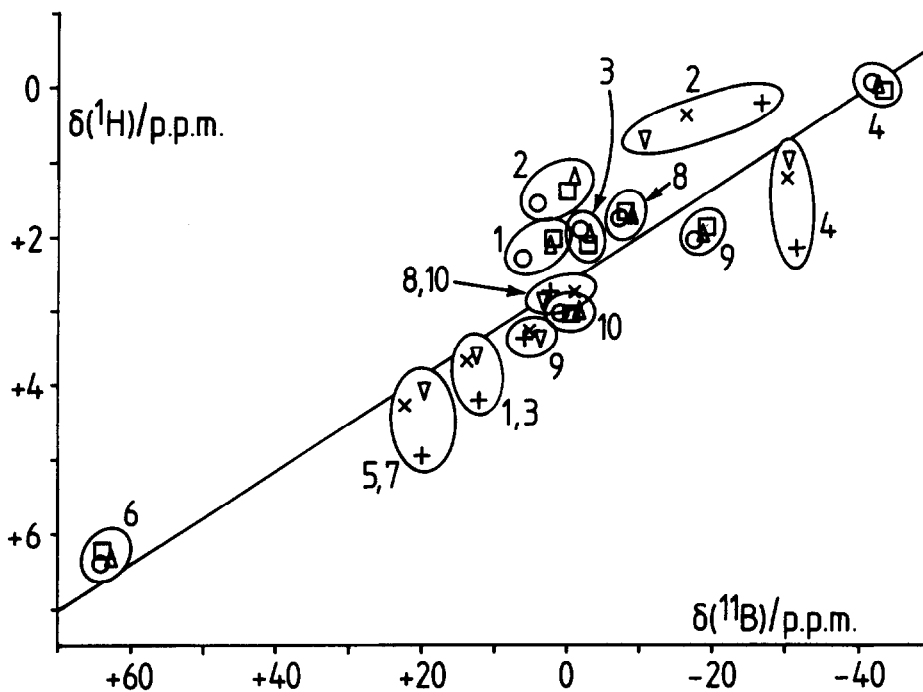


Fig. 5. Plot of boron versus hydrogen nuclear shielding for the *exo*-terminal protons of compounds 1 (×), 2 (+), 3 (Δ), and 4 (□). The other compounds in Tables 1 and 2, viz. [6-(η^5 -C₅Me₅)-*nido*-6-RhB₉H₁₃] (▽) and [5-(η^5 -C₅Me₅)-*nido*-5-RhB₉H₁₁-7-(PMe₂Ph)] (○) (data from refs. 1 and 2) are also included. The line drawn has slope $\delta(^1\text{H})/\delta(^{11}\text{B})$ 1/16 and the cartouches enclose points corresponding to the same structural positions within a particular structural type.

{(PMe₂Ph)₃HRe} and {(PMe₂Ph)₃Os}, to {(PMe₃)₂HIr} [25,26]. Compared to B₁₀H₁₄, these latter only exhibit small shielding changes at the B(2), B(5), and B(7) positions which suggests that excitations involving the arene-metal grouping in the organometallaboranes 1 and 2 reported here may have ultimately to be invoked in molecular orbital treatments of the cluster nuclear shielding.

Two other important aspects of the cluster NMR shielding patterns in compounds 1–4 are illustrated in Fig. 5, which plots $\delta(^1\text{H})$ for the *exo* hydrogen atoms versus $\delta(^{11}\text{B})$ for their directly-bound boron atoms. The first of these, the general parallel between the proton and boron chemical shifts, is now a well-recognized phenomenon [23,24]. In the present case the slope of the correlation, $\delta(^1\text{H})/\delta(^{11}\text{B})$, is ca. 1/16, similar to that observed for a variety of metallaboranes of about this cluster size (for recent examples see refs. 2,3,19,22,25–28). The second aspect is the close grouping of (¹¹B, ¹H) data points for particular structural positions in particular structural types (see individual cartouches in Fig. 5). This close grouping, together with the relative positions of the groups to the line of general correlation, is becoming increasingly useful in assignment and thence as a structural diagnostic (see also refs. 3, 18, 22 and 26). In the work presented here, for example, these considerations remove the ambiguities of assignment in the centrally crowded regions of the spectra between $\delta(^{11}\text{B})$ + 10 and –10 ppm.

Experimental

General. Reactions were carried out under dry nitrogen, using dried and degassed solvents, but subsequent manipulations and separations were carried out in air. $[(C_6Me_6)RuCl_2]_2$ [9] and $[NEt_4][B_9H_{14}]$ [1,29] were made by methods previously reported in the literature [1,9,29], other starting materials being obtained commercially. Preparative thin layer chromatography (TLC) used 1 mm layers of silica (Kieselgel GF54; Fluka) on plates of dimensions 20×20 cm; these were made in the laboratory as required from an acetone slurry, followed by drying in air at ca. $80^\circ C$.

Nuclear magnetic resonance spectroscopy. This was performed at 2.35 and 9.40 Tesla on commercially available instrumentation. The techniques of $^1H\{-^{11}B\}$ spectroscopy [27,29–32], $[^{11}B\{-^{11}B\}]$ -COSY spectroscopy [1–3,22], and $[^1H\{-^1H\}]$ -COSY spectroscopy [3,21,22] were essentially as described elsewhere, particular details being summarized in Table 3. Other NMR spectroscopy was straightforward. Chemical shifts $\delta(^1H)$, $\delta(^{31}P)$, and $\delta(^{11}B)$ are given in ppm to high frequency (low field) of Ξ 100 (SiMe₄), Ξ 40.480 730 (nominally 85% H₃PO₄) and Ξ 32.083 971 MHz (nominally $[BF_3(OEt_2)]$ in $CDCl_3$) [23], respectively.

Mass spectrometry. 70 eV EI-ionization mass spectrometry was carried out on an A.E.I. (now Kratos) MS 30 instrument. FAB-ionization work was carried out using Ar^+ on Kratos MS 80 equipment, using nitrobenzyl alcohol as supporting medium; we thank Dr. Bernard Watson for arranging this.

Preparation of $[6-(\eta^6-C_6Me_6)\text{-}nido\text{-}6\text{-}RuB_9H_{13}]$ (compound 1). $[(\eta^6-C_6Me_6)\text{-}RuCl_2]_2$ (0.1 g; 0.150 mmol) and $[NEt_4][B_9H_{14}]$ (0.145 g; 0.60 mmol) were stirred in CH_2Cl_2 solution (25 cm³) for 18 h. The resulting red solution was reduced in volume (rotary evaporator) and subjected to preparative TLC using CH_2Cl_2 as developing solvent. One predominant product (R_f 0.92) was present as an intense

TABLE 3
EXPERIMENTAL DETAILS FOR 2-DIMENSIONAL NMR EXPERIMENTS

	1	3	3
2D experiment	$[^1H\text{-}^1H]$ -COSY	$[^1H\text{-}^1H]$ -COSY	$[^{11}B\text{-}^{11}B]$ -COSY
Data size	1024, 256	1024, 256	512, 128
$[t_2, t_1$ words]			
Transform size	2048, 1024	2048, 2024	1024, 512
$[F_2, F_1$ words]			
t_2 sweep width	7246	10638	17241
$[= 2 \times t_1$ sweepwidth (Hz)]			
Digital resolution	14.1/2	20.8/2	67/2
$[F_2, F_1$ (Hz/pt)]			
No of transients	80	80	2200
per t_1 increment			
Recycling time	2.07	2.05	0.115
(s)			
Mixing pulse	90	90	45
(deg)			
Window (t_2 and t_1)	sine-bell	sine-bell squared	sine-bell
Other details	$\{^{11}B$ (broad band noise) decoupling; 304 K	$\{^{11}B$ (broad band noise) decoupling; 304 K	$\{^1H$ (broad band noise) decoupling; 298 K

orange-yellow TLC band; this was purified by repeated chromatography and recrystallization from CH_2Cl_2 , and identified as described in the text as [6-(η^6 - C_6Me_6)-*nido*-6-RuB₉H₁₃] (0.088 g; 0.235 mmol; 79%), an orange-yellow crystalline solid. (Found: C, 38.65; H, 8.3; B, 25.65. C₁₂H₃₁B₉Ru calcd.: C, 38.6; H, 8.4; B, 26.0%; $m/e(\text{max})$ (70 eV EI) 378, ¹²C₁₂¹H₃₁¹¹B₉¹⁰⁴Ru calcd.: 378.) Several other chromatographically separable components (colourless, and various shades of yellow, orange, and red) were present in very small yields (\leq ca. 2 mg); some of these were unstable.

*High-yield preparation of [(*p*-cymene)OsCl₂]₂.* A solution of [OsCl₃(OH₂)₃] (1.010 g, 2.88 mmol) in a mixture of α -phellandrene (10 cm³) and degassed ethanol (50 cm³) was heated under reflux for 3.5 h, affording a green solution. This was cooled, reduced in volume under reduced pressure, and column-chromatographed on silica, using ethanol as eluting medium. The eluant was reduced in volume to ca. 10 cm³ under reduced pressure. Addition of light petroleum resulted in the precipitation of [(*p*-cymene)OsCl₂]₂ [33] as a dark yellow-green microcrystalline powder, which was washed with diethyl ether and dried in vacuo, yield 1.015 g; 1.28 mmol; 89%. (Found: 30.9; H, 3.7; and Cl, 17.9. C₂₀H₂₈Cl₄Os₂ calcd.: C, 30.4; H, 3.6, and Cl, 17.9%.)

Preparation of [(η^6 -C₆Me₆)OsCl₂]₂. [(*p*-Cymene)OsCl₂]₂ (3.52 g; 4.45 mmol) was heated in hexamethylbenzene (40 g) at 180 °C with stirring for 5.5 h. The reaction mixture was cooled and ground with analytical filter aid (cellulose powder) and placed in a Soxhlet extractor. Hexamethylbenzene and unreacted [(*p*-cymene)OsCl₂]₂ were then removed by extraction with diethyl ether, the unreacted [(*p*-cymene)OsCl₂]₂ (1.148 g; 1.45 mmol; 32% recovery) being recovered via this extract by sublimation in vacuo. Continued Soxhlet-extraction of the reaction mixture with dichloromethane yielded a red-brown solution. Column-chromatography of this solution on silica, initially using acetonitrile as eluting medium, and then acetone, afforded [(C₆Me₆)OsCl₂]₂ as a mustard-yellow microcrystalline compound (1.008 g; 1.19 mmol; 26.7% overall, 39.7% based on [(*p*-cymene)OsCl₂]₂ consumed) that could be crystallized from acetone or dichloromethane (although some decomposition occurs in the latter). (Found: C, 33.45; H, 4.20; Cl, 17.8. C₂₄H₃₆Cl₄Os₂ calcd.: C, 34.0; H, 4.28; Cl, 16.7%). NMR: $\delta(^1\text{H}) + 2.02$ ppm (CDCl₃ solution at 294 K). IR: $\nu_{\text{max}}(\text{Os}-\text{Cl})$ 260, 305 cm⁻¹ (Nujol). Mass spectr.: $m/e(\text{max})$ 801–821 corresponding to [C₂₄H₃₆Cl₃Os₂]⁺ observed using FAB-ionization mass spectrometry with the relative intensities in this parent ion isotopomer envelope corresponding to those calculated for the natural abundancies of the constituent elements. 70-eV EI ionization exhibited $m/e(\text{max})$ 428 corresponding to [¹²C₁₂¹H₁₈³⁷Cl₂¹⁹²Os]⁺.

*Preparation of [6-(η^6 -C₆Me₆)-*nido*-6-OsB₉H₁₃] (compound 2).* A procedure exactly analogous to that used for the ruthenium compound **1** was followed, but using [(η^6 -C₆Me₆)OsCl₂]₂ (prepared as described in the preceding paragraph) instead of [(η^6 -C₆Me₆)RuCl₂]₂. This resulted in the isolation of [6-(η^6 -C₆Me₆)-*nido*-6-OsB₉H₁₃] (compound **2**, 13% yield) as an orange crystalline solid, identified as such as described in the text [$m/e(\text{max})$ (70 eV EI) 466, ¹²C₁₂¹H₃₁¹¹B₉¹⁹²Os calcd.: 466].

*Preparation of [5-(η^6 -C₆Me₆)-*nido*-RuB₉H₁₁-7-(PMe₂Ph)] (compound 3).* A solution of compound **1** (0.08 g; 0.214 mmol) and PMe₂Ph (0.030 g; 0.217 mmol) in CH₂Cl₂ solution (ca. 25 cm³) was heated under reflux for 4 h. The solution was reduced in volume and subjected to preparative TLC using CH₂Cl₂ as developing medium. The predominant component (R_f 0.46) was purified by repeated chro-

matography and recrystallisation from CH_2Cl_2 and identified as described in the text as [5-($\eta^6\text{-C}_6\text{Me}_6$)-*nido*-5-RuB₉H₁₁-7-(PMe₂Ph)] (compound **3**), a yellow crystalline solid (0.084 g; 0.165 mmol; 77%). (Found C, 48.3; H, 7.9; B, 17.85; P, 6.0%. C₂₀H₄₀B₉PRu calcd: C, 47.1; H, 7.85, B, 19.1, P, 6.1%; *m/e*(max) (70 eV) 514, ¹²C₂₀¹H₄₀¹¹B₉³¹P¹⁰⁴Ru calcd.: 514.) Other components of the reaction mixtures were identified as compound **1** (ca. 5 mg; 6% recovery) and *arachno*-[B₉H₁₃(PMe₂Ph)] (ca. 2 mg), identified by NMR spectroscopy.

*Preparation of [5-($\eta^6\text{-C}_6\text{Me}_6$)-*nido*-5-RuB₉H₁₁-7-(PPh₃)] (compound **4**).* A procedure analogous to that used for the preparation of compound **3** was followed, but using PPh₃ instead of PMe₂Ph. This resulted in the isolation of [5-($\eta^6\text{-C}_6\text{Me}_6$)-*nido*-5-RuB₉H₁₁-7-(PPh₃)] (compound **4**, 54% yield, TLC: *R_f* 0.64 using CH₂Cl₂) as an orange crystalline solid, identified by analogy with compound **3** and as described in the text [*m/e*(max) (70 eV EI) 638; ¹²C₃₀¹H₄₄¹¹B₉³¹P¹⁰⁴Ru calcd.: 638].

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